*Pestic. Sci.* 1996, **48**, 219–223

# Analysis of Fenoxaprop-Ethyl and Fenoxaprop in Drinking Water Using Solid-Phase Extraction and Ion-Pair HPLC

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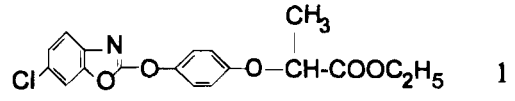
(Received 26 October 1995; revised version received 19 March 1996; accepted 6 June 1996)

**Abstract:** A method for simultaneous analysis of fenoxaprop-ethyl and its main metabolite fenoxaprop in drinking water is described. C-18 solid-phase extraction was used for pre-concentration of the analytes. Two different approaches for increasing the retention of the acidic metabolite by reversed-phase solid-phase extraction were studied: ionization suppression at low pH and ion-pairing with addition of triethylamine. The advantage of applying the ion-pairing mechanism is discussed with respect to higher recoveries obtained for fenoxaprop-ethyl. High-performance liquid chromatography with a UV detector operating at 240 nm was used for separation and detection of both compounds. Ion-pairing elution technique was applied on a C-18 reversed-phase column. The sensitivity, linearity and repeatability of the method were evaluated. The limit of determination of this method, for parent compound and metabolite, is sufficiently low for it to be used to test water samples for compliance with the European Union Drinking Water Directive.

Key words: pesticide residues, HPLC, SPE, ion-pairing, drinking water

## 1 INTRODUCTION

Fenoxaprop-ethyl (ethyl (±)-2[4-(6-chlorobenzoxazol-2-yloxy)phenoxy]propanoate; Fig. 1, **1**) is a selective herbicide, widely used for post-emergence control of a broad spectrum of grass weeds in dicotyledonous crops.[1] Rapid hydrolysis to the corresponding acid, fenoxaprop (**2**), has been observed in plants and environment.[2,3] As fenoxaprop, due to its acidic character, is considered a probable leacher through the soil, the increasing use of the parent herbicide may pose problems for ground water resources. The high toxicity to fish ($LC_{50}$ 0·5 mg $kg^{-1}$) of fenoxaprop indicates a potential risk from water contamination.[4]

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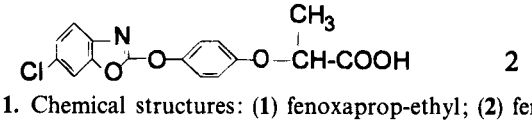


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**Fig. 1.** Chemical structures: (**1**) fenoxaprop-ethyl; (**2**) fenoxaprop.

Analytical methods for the determination of fenoxaprop-ethyl and its main metabolite in biological materials and soil using gas chromatography with electron-capture detector after derivatization have been described.[5] HPLC with chiral stationary phases has been used for selective determination of the enantiomers of fenoxaprop-ethyl and fenoxaprop in soil.[2] C-18 reversed-phase HPLC and gradient elution with acidified mobile phase have been applied to the simultaneous analysis of both compounds in the soil.[6] Analytical methods adequate for the determination of the parent compound and its hydrolysis product in water have not been reported.

The aim of this work was to develop a method for the simultaneous determination of fenoxaprop-ethyl and fenoxaprop in drinking water at levels of 0·1 μg $litre^{-1}$; to establish adequate pre-concentration procedures by comparative study of different approaches in reversed-phase solid-phase extraction with respect to their influence on recovery; to determine conditions for HPLC separation and sensitive detection of both compounds.



*Pestic. Sci.* 0031-613X/96/$09.00 

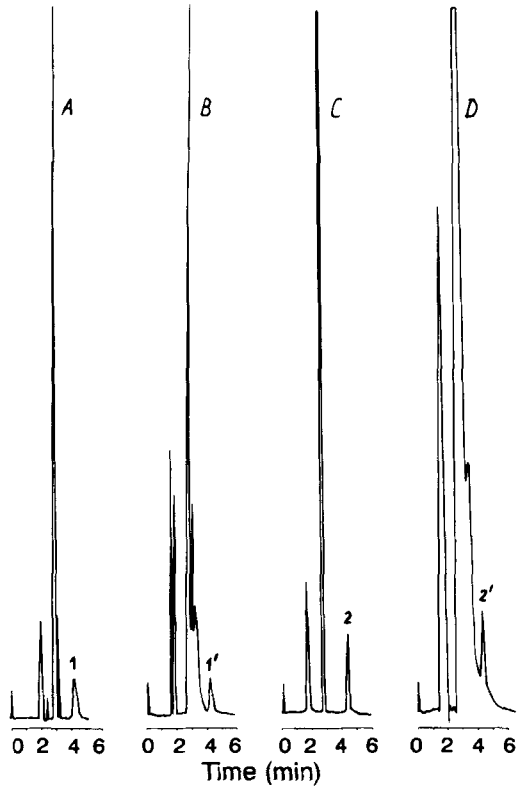


**Fig. 2.** HPLC chromatograms obtained under conditions described in Section 2.3. Attenuation 0·02 AUFS. (A) Working standard solution of fenoxprop, 2 ng (peak 1); mobile phase A + B (6 + 4). (B) Tap water sample fortified with fenoxaprop-ethyl, 2 ng and FP, (peak 1'); mobile phase A + B (6 + 4). (C) Working standard of fenoxaprop-ethyl, 2 ng (peak 2); mobile phase A. (D) Tap water sample fortified with fenoxaprop-ethyl, 2 ng (peak 2') and fenoxaprop 2 ng; mobile phase A.

## 2 EXPERIMENTAL METHODS

### 2.1 Chemicals

All reagents and chemicals were of analytical grade. Analytical grade methanol and bidistilled water were used for HPLC.

Triethylamine was obtained from Merck (D-6100 Darmstadt, Germany) and 500 mg C-18 silica Sep-Pak cartridges from Waters (Millipore, Milford 01757 USA). Fenoxaprop-ethyl analytical standard was from Dr Ehrenstorfer (D-8900 Augsburg, Germany). As fenoxaprop was not commercially available, it was prepared by acid hydrolysis of fenoxaprop-ethyl after Celi *et al.*[6] Fenoxaprop-ethyl (500 mg) was refluxed with hydrochloric acid (6 M; 100 ml) for 2 h. The acidic solution was extracted with dichloromethane (3 × 20 ml) and the solvent was evaporated under a gentle stream of nitrogen. The residue was dissolved in methanol. The concentrated solution, equivalent to 1 mg $ml^{-1}$, was chromatographed under the conditions described in Section 2.3 for the determination of fenoxaprop-ethyl. No peak was observed with a retention time corresponding to the parent compound at limit of detection 0·025 $\mu g\ ml^{-1}$. This was a confirmation that the hydrolysis of fenoxaprop-ethyl was complete. The hydrolyzed product was not retained on a C-18 column under neutral pH of the mobile phase. Sufficient retention was achieved under pH < 3, thus indicating that it was an acidic compound. The UV-absorption spectra of fenoxaprop-ethyl and fenoxaprop were similar, with two maxima, at 235 and 280 nm. The absorbance at 235 nm was higher. A wavelength near the first maximum (240 nm) was selected for HPLC determination as the sensitivity of detection was close to the maximum but the effect of co-eluting compounds was lower than at 235 nm. Stock standard solutions (1 mg $ml^{-1}$) were prepared in methanol. Working standard solutions were prepared by diluting with HPLC mobile phase. HPLC mobile phase: 0·01 M triethylamine buffer was prepared by dissolving triethylamine (1·4 ml) in bidistilled water (1 litre) and adjusting the pH to 6·5 with sulfuric acid (0·5 M). Mobile phase A was a mixture of methanol + triethylamine buffer (9 + 1 by volume); mobile phase B was a mixture of methanol + triethylamine buffer (4 + 6 by volume).

### 2.2 Water extraction

Aqueous samples were fortified with known volumes of standard solutions. Two ways of increasing the retention of fenoxaprop were studied.

*2.2.1 Adjusting the pH of water samples at 2*

Fortified water samples (0·5–1 litre) were acidified with sulfuric acid (0·5 M) to *c.* pH 2. Methanol (1 ml) was added to each 1-litre sample to ensure solvation of the C-18 chains.

*2.2.2 Addition of ion-pairing reagent to water samples*

Triethylamine was added as ion-pairing reagent to give a concentration of 0·01 M in water samples. The samples were adjusted to pH 6·5 with sulfuric acid (0·5 M). After the addition of 1 ml of methanol the samples were preconcentrated by solid-phase extraction.

*2.2.3 Solid-phase extraction*

The Sep-Pak cartridges were conditioned with methanol (10 ml) and washed with water (10 ml). The samples were forced to pass through the cartridge under vacuum at a rate of *c.* 10 ml $min^{-1}$. The sorbent bed was washed with distilled water (5 ml) and dried under vacuum for about 30 min. Analytes were eluted with methanol (1 ml). When it was necessary to eliminate the influence of early eluting matrix extractants, the sorbent was washed first with methanol + triethylamine buffer

**TABLE 1**

Comparison of Fenoxaprop-Ethyl and Fenoxaprop Recoveries Obtained by Two Different Approaches of Solid-Phase Extraction from 0·5 litre of Tap Water at Level of Fortification 0·5 μg litre$^{-1}$ (number of samples, $n = 4$)

| | *pH 2* | | *Triethylamine buffer at pH 6·5* | |
|---|---|---|---|---|
| *Compound* | *Recovery (%)* | *Mean (%)* | *Recovery (%)* | *Mean (%)* |
| Fenoxaprop-ethyl | 32·3 | | 83·2 | |
| | 52·7 | | 84·9 | |
| | 70·0 | 51·5 | 95·1 | 86·8 |
| | 52·6 | | 83·9 | |
| | 50·0 | | | |
| Fenoxaprop | 101·5 | | 91·9 | |
| | 95·5 | 95·7 | 85·2 | 90·8 |
| | 91·9 | | 97·4 | |
| | 93·8 | | 88·5 | |

(1 + 1; 1·5 ml), the eluate was discarded and the analytes were eluted with methanol (1·5 ml). The methanol was evaporated under a gentle stream of nitrogen and the residue dissolved in a mixture of methanol + triethylamine buffer (1 + 1) to a final volume of 0·5 ml.

### 2.3 HPLC analysis

HPLC analysis was performed with a Pye Unicam liquid chromatograph equipped with a PU 4010 pump, a PU variable wavelength UV detector and a Rheodyne Model 7125 injector with a 20-μl loop. A

**TABLE 2**

Recoveries of Fenoxaprop-Ethyl and Fenoxaprop from Drinking Waters Fortified at Different Levels of Concentrations and Analyzed under the Experimental Conditions (number of samples, $n = 3$)

| | *Fenoxaprop-ethyl* | | | *Fenoxaprop* | | |
|---|---|---|---|---|---|---|
| *Sample* | *Fortification (μg litre$^{-1}$)* | *Recovery (%)* | *Mean (%)* | *Fortification (μg litre$^{-1}$)* | *Recovery (%)* | *Mean (%)* |
| Tap water A | | 102·1 | | | 94·5 | |
| | 0·2 | 89·4 | 89·8 | 0·4 | 77·2 | 87·8 |
| | | 78·0 | | | 91·7 | |
| | | 98·3 | | | 77·6 | |
| | 1·0 | 95·7 | 93·5 | 1·0 | 62·8 | 73·3 |
| | | 86·5 | | | 79·4 | |
| Tap water B | | 80·6 | | | 85·7 | |
| | 0·2 | 87·1 | 82·1 | 0·4 | 64·3 | 74·2 |
| | | 78·5 | | | 72·7 | |
| | | 82·3 | | | 88·0 | |
| | 1·0 | 80·7 | 84·0 | 1·0 | 80·1 | 87·1 |
| | | 89·2 | | | 93·3 | |
| Well water | | 80·9 | | | 78·6 | |
| | 0·1 | 71·4 | 74·1 | 0·2 | 68·4 | 75·3 |
| | | 70·0 | | | 78·9 | |
| | | 78·2 | | | 75·8 | |
| | 0·2 | 86·7 | 81·6 | 0·4 | 72·7 | 77·1 |
| | | 80·0 | | | 82·9 | |
| | | 85·8 | | | 83·4 | |
| | 1·0 | 79·2 | 86·8 | 1·0 | 102·7 | 91·2 |
| | | 95·4 | | | 87·5 | |

TABLE 3
Recoveries of Fenoxaprop-Ethyl and Fenoxaprop from Drinking Water Fortified at Different Levels of Concentrations and Analyzed with Fractional Elution from Solid-Phase Extraction Cartridges (number of samples, $n = 3$)

| | *Fenoxaprop-ethyl* | | | *Fenoxaprop* | | |
|---|---|---|---|---|---|---|
| *Sample no.* | *Fortification* ($\mu g\ litre^{-1}$) | *Recovery* (%) | *Mean* (%) | *Fortification* ($\mu g\ litre^{-1}$) | *Recovery* (%) | *Mean* (%) |
| 1 | | 71·4 | | | 80·8 | |
| 2 | 0·1 | 76·2 | 69·8 | 0·2 | 73·1 | 82·1 |
| 3 | | 61·9 | | | 92·3 | |
| 4 | | 90·3 | | | 89·7 | |
| 5 | 1 | 86·2 | 88·2 | 1 | 91·8 | 88·3 |
| 6 | | 88·3 | | | 83·5 | |

250 mm × 4·6 mm ID column Lichrosorb RP-18 (5 $\mu$m; Merck) was used. Fenoxaprop was eluted with mobile phase A + B (6 + 4 by volume) at a flow-rate of 1 ml $min^{-1}$ for 4·2 min. Fenoxaprop-ethyl was eluted for 4·4 min with mobile phase A at the same flow-rate. Typical chromatograms are shown in Fig. 2.

## 3 RESULTS AND DISCUSSION

Fenoxaprop-ethyl and its metabolite fenoxaprop differ in their retention capacity in solid-phase extraction. As a neutral compound, fenoxaprop-ethyl is easily retained by C-18 phase. Fenoxaprop does not adsorb strongly to a reversed-phase support. The retention of an ionic compound depends on its ionization state. As a rule the approach, reported in the literature, to increase the retention of acidic compounds in reversed-phase chromatography is by adjusting the pH to below the $pK_a$ value of the acids.[7] Application of ion-pairing mechanism in reversed-phase HPLC of ionic pesticides has been reported in a limited number of papers.[8] Application of ion-pairing in reversed-phase solid-phase extraction has not been reported in the literature accessible to us.

When strongly acidic conditions were used in the solid-phase extraction of fenoxaprop-ethyl and fenoxaprop, good recoveries of the acidic metabolite were obtained, but recoveries of the parent compound were not acceptable (Table 1). The probable reason was a partial hydrolysis of the compound. To avoid the loss of the ester, solid-phase extraction was carried out under mild conditions at pH 6·5 in the presence of triethylamine as ion-pairing reagent. As is shown in Table 1, under these conditions the acidic compound was sorbed by C-18 phase, resulting in good recoveries. At the same time the recoveries of fenoxaprop-ethyl were improved significantly.

The recoveries of fenoxaprop and fenoxaprop-ethyl were determined at different levels of fortification in three types of drinking water—a very soft water (tap water A), a soft water (well water) and a medium-hard water (tap water B). The recovery experiments were carried out in triplicate for each fortification level and type of water. The results are reported in Table 2. Analysis of unspiked drinking water samples indicated that no coextractives with the same retention times as fenoxaprop-ethyl and fenoxaprop were eluted. In some highly polluted water samples the early eluted components from the sample matrix may overlap with the peaks of fenoxaprop-ethyl. Fractional elution from solid-phase extraction cartridges was an adequate solution in such cases. The C-18 cartridges were eluted first with a portion of weak solvent to elute the early desorbed impurities. The eluates were discarded. Then the analytes were eluted with the stronger solvent sufficient for their quantitative desorbtion as described in Section 2.3. The results of recovery experiments carried out with fractional elution are presented in Table 3.

The sensitivity obtained under the experimental conditions described is characterized by the minimum detectable amounts (signal-to-noise ratio 3 : 1) of the analytes injected as standard mixtures and the limits of determination of the method with both compounds (Table 4).

The response of the detector is linear over a wide range of concentrations. Standard curves are presented

TABLE 4
Sensitivity of the Method

| *Compound* | *Minimum detectable amount (ng)* | *Limit of determination* ($\mu g\ litre^{-1}$) |
|---|---|---|
| Fenoxaprop-ethyl | 0·5 | 0·05 |
| Fenoxaprop | 1·0 | 0·1 |

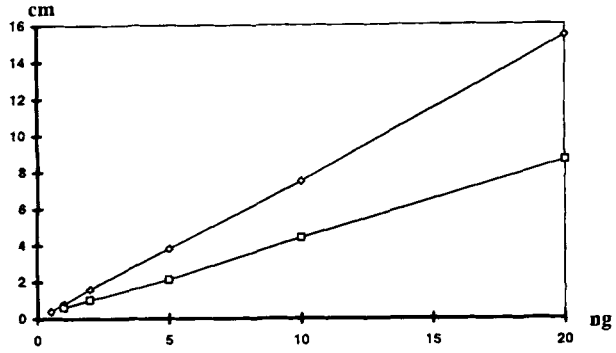


**Fig. 3.** Calibration curves: response (cm peak height) as a function of amount (ng) for (◇) fenoxaprop-ethyl and (□) fenoxaprop.

in Fig. 3. Correlation coefficients within the range of operation are higher than 0·998.

The method developed has a good reliability and sufficient sensitivity. It is applicable to simultaneous determination of the parent compound of the modern herbicide fenoxaprop-ethyl and its main metabolite fenoxaprop acid in drinking waters for monitoring compliance with the European Union Drinking Water Directive.[9]

## 4 CONCLUSION

Utilizing the ion-pairing mechanism in reversed-phase HPLC separation of the compounds analyzed demonstrated advantages in comparison with the ionization suppression in the presence of acid modifiers. A mobile phase containing triethylamine buffer was preferred in the HPLC separation and elution as it provided more favourable conditions for faster background equilibration. On the other hand, working at pH near to neutral prevented a decrease of the column life. Application of triethylamine as ion-pairing reagent has proved to be effective also in pre-concentration of both fenoxaprop-ethyl and fenoxaprop acid by reversed-phase solid-phase extraction from water samples. This approach provided milder conditions of analysis and prevented hydrolysis during the pre-concentration step of susceptible compound such as fenoxaprop-ethyl. The good recoveries and repeatability obtained with different types of drinking water samples as well as the sufficient sensitivity confirm that the procedure developed can be considered efficient for monitoring studies of drinking waters.

## ACKNOWLEDGEMENT

Financial support from the Commission of the European Communities (Contract No ERB CIPDCT 925097) is greatly appreciated.

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